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PATENT SPECIFICATION

788,931

Inventors:—ANDRE PACOUD, JACQUES DALLEMAGNE, and ALBERT MERCIER.



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COMPLETE SPECIFICATION.

Improvements in or relating to the Separation of Organic Mixtures.

We, SOCIETE DES USINES CHIMIQUES RHÔNE-POULENC, a French Body Corporate, of 21 Rue Jean-Goujon, Paris, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

10 The present invention is for improvements in or relating to the separation of organic mixtures and more particularly concerns a process for the separation of the components of mixtures of one or more aliphatic monocarboxylic acids with water and formaldehyde, which mixtures may also contain ketones of lower boiling point than the acid or acids.

20 The invention is especially directed to the separation of the components of mixtures of formic acid, acetic acid, water and formaldehyde, which may in addition contain acetone; such materials being for example as obtained by the catalytic oxidation of acetone by means of molecular oxygen. The separation from one another, even in only a technical state of purity, of the components of such mixtures cannot be carried out without employing complicated means involving a considerable expenditure of heat.

30 It is the principal object of the present invention to produce from mixtures as aforesaid, in a simple manner and without a considerable expenditure of heat, (a) anhydrous acid or acids substantially free from formaldehyde and ketone (when present), (b) an aqueous formaldehyde solution substantially free from acid, and (c) ketone (when present) substantially free from formaldehyde and acid. It is a further object of this invention, in the case of mixtures resulting from the catalytic oxidation of

acetone, to provide a process for the recovery of the anhydrous acids free from formaldehyde and acetone (thus facilitating the subsequent separation of the individual acids), an aqueous solution of formaldehyde free from acidity, and finally acetone containing only traces of formaldehyde.

45 The present invention broadly comprises a process for the separation of useful products from a mixture of one or more aliphatic monocarboxylic acids, water and formaldehyde, wherein the said mixture is subjected to rectification in a distillation column in the presence of an auxiliary organic liquid whereby to form an azeotropic mixture having a boiling point lower than that of said acid or acids, said auxiliary liquid being substantially insoluble in water and being capable of forming with water and formaldehyde, but not with said acid or acids, said azeotropic mixture, recovering substantially anhydrous acid or acids from the base of the column, condensing the vapour phase of the column to a heterogeneous liquid phase wherein substantially all the formaldehyde is in the form of a substantially acid-free aqueous solution and separating said aqueous formaldehyde solution therefrom.

50 The term "auxiliary organic liquid" is used to mean a substance which has the properties just recited therefor. Examples of auxiliary organic liquids are such ethers as di-isopropyl ether and di-butyl ether, such esters as iso-propyl and butyl formates and acetates and such ketones as methyl iso-propyl ketone and methyl isobutyl ketone.

55 When rectification is effected in the manner hereinbefore described, a ternary azeotropic mixture (auxiliary organic liquid-formaldehyde-water) forms utilising the water in the system and distils off, leaving practically anhydrous acid or acids in the still. The

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condensation of the compounds of the azeotropic mixture gives a distillate which on standing separates into two layers, the lower aqueous layer containing the formaldehyde and but a minor proportion of auxiliary organic liquid and the upper layer consisting almost wholly of auxiliary organic liquid. If there is not sufficient water in the initial mixture to obtain the formaldehyde in the desired concentration, the additional quantity of water required may be introduced either into the feed mixture or at any suitably chosen point of the distillation column. The process of the invention may be applied to the separation of aqueous mixtures which contain, in addition to the acid(s) and formaldehyde, a ketone having a boiling point lower than that of those of the acid or acids present. Such a ketone is acetone. When the process is so applied, the choice of auxiliary organic liquid to be employed is more restricted, since it must not only possess the characteristics hereinbefore referred to but must also be incapable of forming either a binary azeotrope with the ketone or a ternary azeotrope with the ketone and the water present and the boiling point of the azeotropic mixture which it forms with formaldehyde and water must be between that of the ketone and that of the acid or (where more than one acid is present) of the acid of lower or lowest boiling point. This restricted group of auxiliary organic liquid is hereinafter referred to as "ketone auxiliary organic liquids". Examples of ketone auxiliary organic liquids are isopropyl formate and isopropyl acetate. Using a ketone auxiliary organic liquid, it is possible to obtain the ketone free from formaldehyde by introducing at a suitably chosen point in the rectifying column, situated in the lower part of the ketone concentration zone, a quantity of water sufficient to displace the formaldehyde towards the plates situated below this zone. The water thus introduced may be that which (as already mentioned), it may be necessary to introduce in order to obtain the formaldehyde solution in the desired concentration. It was already known to dehydrate an aliphatic carboxylic acid or a mixture of a number of aliphatic carboxylic acids by means of azeotropic processes, but it was not obvious that such processes would be applicable to complex aqueous mixtures of the said acids with formaldehyde and to such mixtures as also contain ketones, and the fact that all the formaldehyde is collected in the aqueous phase of the azeotropic distillate is a novel and unexpected effect. The process of the present invention is preferably effected in an apparatus arranged for continuous operation, such apparatus comprising a rectifying still having a vertical column provided with a spaced series of baffle plates of perforated plate, "bubble-cap" or other conventional form, a feed mixture inlet situated at about midway of the column, an acid collecting chamber at the bottom of the column fitted with appropriate heating means and a vapour outlet at the top of the column. The vapour outlet is connected to a condenser feeding condensate to the mid-section of a decanter tank, fitted with two outlet conduits, one at the top, which is connected to the top of the rectifying column, for draw-off and return to the column of auxiliary organic liquid and the other at the bottom for draw-off of formaldehyde solution. When a ketone is present in the feed mixture, it collects in the decanting tank and is removed with the formaldehyde. It is however, possible to remove substantially pure ketone by equipping the column for fractional distillation such that the ketone vapour is withdrawn from the top of the column and the less volatile azeotropic mixture vapour is withdrawn at a point intermediate the feed mixture inlet and the ketone vapour outlet. To achieve substantially complete separation of ketone and formaldehyde under these conditions, it is preferred, if necessary, to adjust the quantity of water in the system so that it takes up all of the formaldehyde present. Any water required for this purpose is introduced at a point above the azeotrope condensation zone. It is usually convenient to introduce the auxiliary substance into the system separately from the feed mixture to be separated but it can be added to the feed mixture before-hand if desired. The invention is illustrated by the following Examples; the percentages are by weight.

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EXAMPLE I.
A mixture containing :
 90.4% of acetic acid
 4.5% of formic acid
 1.0% of formaldehyde
 4.1% of water

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is introduced into a column provided at the top with a condenser and a decanting system. In the column there is introduced isopropyl ether intended to serve as auxiliary organic liquid. A heterogeneous aqueous phase is condensed at the top and decants. The aqueous mixture contains 23.2% of formaldehyde, 0.3% of isopropyl ether and 0.01% of acids; the organic phase is returned into the column. At the bottom of the column, a mixture of formic acid and acetic acid containing only 0.03% of formaldehyde and 0.05% of water is withdrawn. The acids of this mixture can be separated from one another by known means.

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EXAMPLE II.
Into a column provided with a decanting

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plate at a point midway of its height is introduced a mixture composed of:

5 55.4% of acetic acid
 13.5% of formic acid
 18.0% of acetone
 6.7% of formaldehyde
 6.4% of water.

10 The column is charged with isopropyl acetate, as ketone auxiliary organic liquid. The mixture is introduced at the centre of the lower part of the column at the rate of 7 kg. per hour. 2 litres of water per hour are introduced at the middle of the upper part.

15 1.150 kg. of acetone containing neither isopropyl acetate nor acids, and only 0.2% of formaldehyde and 0.2% of water are withdrawn per hour at the top of the column.

20 On the decanting plate, there are separated the isopropyl acetate which returns into the column, and an aqueous layer containing 15% of formaldehyde, 3% of acetone, 2% of isopropyl acetate and at most 0.05% of acids. From this mixture a pure formaldehyde solution can readily be obtained.

25 At the bottom of the column, 4.91 kg. per hour of the mixture of formic acid and acetic acid containing only 0.1% of water and 0.05% of formaldehyde are withdrawn, from which mixture the pure formic acid and the pure acetic acid can be separated without difficulty.

What we claim is:—

30 1. A process for the separation of useful products from a mixture of one or more aliphatic monocarboxylic acids, water and formaldehyde which comprises subjecting the said mixture to rectification in a distillation column in the presence of an auxiliary organic liquid whereby to form an azeotropic mixture having a boiling point lower than that of said acid or acids, said auxiliary liquid being substantially insoluble in water and being capable of forming with water and formaldehyde, but not with said acid or

acids, said azeotropic mixture, recovering substantially anhydrous acid or acids from the base of the column, condensing the vapour phase of the column to a heterogeneous liquid phase wherein substantially all the formaldehyde is in the form of a substantially acid-free aqueous solution and separating said aqueous formaldehyde solution therefrom.

50 2. A process according to Claim 1 wherein the mixture also contains a ketone of boiling point lower than the acid or acids present, the auxiliary organic liquid is one which is incapable of forming a binary azeotrope with the said ketone or a ternary azeotrope with the said ketone and water, but which forms an azeotropic mixture with formaldehyde and water having a boiling point greater than that of the ketone but lower than that of the lowest boiling acid present in the mixture, and the ketone is separately recovered substantially free from formaldehyde.

60 3. A process according to Claim 1 wherein the vapour phase containing water, formaldehyde and auxiliary organic liquid is withdrawn from the top of the column.

65 4. A process according to Claim 2 wherein the rectification is effected in a vertical distillation column provided with a decanting plate about midway of its height, the acid or acids are withdrawn from the base of the column, a mixture consisting of formaldehyde and water with traces of ketone and acid is withdrawn at the decanting plate, and substantially pure ketone is withdrawn at the top of the column.

70 5. Processes for the separation of mixtures of aliphatic monocarboxylic acid, water and formaldehyde, and optionally ketone, into useful individual compounds, substantially as hereinbefore described.

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PROVISIONAL SPECIFICATION.

Improvements in or relating to the Separation of Organic Mixtures.

We, SOCIETE DES USINES CHIMIQUES RHONE-POULENC, a French Body Corporate, of 21 Rue Jean-Goujon, Paris, France, do hereby declare this invention to be described in the following statement:—

80 The present invention is for improvements in or relating to the separation of organic mixtures and more particularly concerns a process for the separation of the components of mixtures of one or more aliphatic monocarboxylic acids with water and form-

100 aldehyde, which mixtures may also contain ketones of lower boiling point than the acid or acids.

105 The invention is especially directed to the separation of the components of mixtures of formic acid, acetic acid, water and formaldehyde, which may in addition contain acetone; such materials being for example as obtained by the catalytic oxidation of acetone by means of molecular oxygen. The separation from one another, even in only a technical

state of purity, of the components of such mixtures cannot be carried out without employing complicated means involving a considerable expenditure of heat.

5 It is the principal object of the present invention to produce from mixtures as aforesaid, in a simple manner and without a considerable expenditure of heat, (a) anhydrous acid or acids substantially free from formaldehyde and ketone (when present), (b) an aqueous formaldehyde solution substantially free from acid, and (c) ketone (when present) substantially free from formaldehyde and acid. It is a further object of 10 this invention, in the case of mixtures resulting from the catalytic oxidation of acetone, to provide a process for the recovery of the anhydrous acids free from formaldehyde and acetone (thus facilitating the subsequent separation of the individual acids), an aqueous solution of formaldehyde free from acidity, and finally acetone containing only traces of formaldehyde.

The present invention broadly comprises a 25 process for the separation from mixtures of one or more aliphatic monocarboxylic acids with water and formaldehyde, of the acid or mixture of acids in substantially anhydrous and formaldehyde-free state and of the 30 formaldehyde in the form of a substantially acid-free aqueous solution, wherein the initial mixture is rectified in the presence of an auxiliary product as hereinafter defined.

The term "auxiliary product" as used 35 herein means a substance which is practically insoluble in water and forms with water, but not with the said anhydrous acid or acids, an azeotropic mixture having a boiling point lower than that of the said acid or of the 40 said acids. Examples of auxiliary products are such ethers as di-isopropyl ether and di-butyl ether, such esters as isopropyl and butyl formates and acetates and such ketones as methyl isopropyl ketone and 45 methyl isobutyl ketone.

When rectification is effected in the manner hereinbefore described, a ternary azeotropic mixture (auxiliary product-formaldehyde-water) forms utilising the water in the 50 system and distil off, leaving practically anhydrous acid or acids in the still. The condensation of the compounds of the azeotropic mixture gives a distillate which on standing separates into two layers, the lower 55 aqueous layer containing the formaldehyde and but a minor proportion of auxiliary product and the upper layer consisting almost wholly of auxiliary product.

If there is not sufficient water in the 60 initial mixture to obtain the formaldehyde in the desired concentration, the additional quantity of water required may be introduced either into the feed mixture or at any suitably chosen point of the distillation 65 column.

The process of the invention may be applied to the separation of aqueous mixtures that in addition to the acid(s) and formaldehyde also contain a ketone having a boiling point lower than that of the acid or acids present. Such a ketone is acetone. When the process is so applied, the choice of auxiliary product to be employed is more restricted, that is to say it must not only possess the characteristics hereinbefore referred to but must also be incapable of forming either a binary azeotropic with the ketone or a tertiary azeotropic with the ketone and the water present and the boiling point of the azeotropic mixture which it does form must be between that of the ketone and that of the acid or (where more than one acid is present) of the acid of lower or lowest boiling point. Such restricted class of auxiliary products is herein-after referred to as "ketone auxiliary products". Examples of ketone auxiliary products are isopropyl formate and isopropyl acetate. Using a ketone auxiliary product, it is possible to obtain the ketone free from formaldehyde by introducing at a suitably chosen point in the rectifying column, situated in the lower part of the ketone concentration zone, a quantity of water sufficient to displace the formaldehyde towards the plates situated below this zone. The water thus introduced may be that which (as already mentioned), it may be necessary to introduce in order to obtain the formaldehyde solution in the desired concentration.

It was already known to dehydrate an aliphatic carboxylic acid or a mixture of a number of aliphatic carboxylic acids by means of azeotropic processes, but it was not obvious that such processes would be applicable to complex aqueous mixtures of the said acids with formaldehyde and to such mixtures as also contain ketones, and the fact that all the formaldehyde is collected in the 100 aqueous phase of the azeotropic distillate is a novel and unexpected effect.

The process of the present invention is preferably effected in an apparatus arranged for continuous operation, such apparatus 115 comprising a rectifying still having a vertical column provided with a spaced series of baffle plates of perforated plate, "bubble-cap" or other conventional form, a feed mixture inlet situated at about midway 120 of the column, and acid collecting chamber at the bottom of the column fitted with appropriate heating means and a vapour outlet at the top of the column. The vapour outlet is connected to a condenser feeding 125 condensate to the mid-section of a decanter tank, fitted with two outlets conduits, one at the top, which is connected to the top of the rectifying column, for draw-off and return to the column of auxiliary product 130

and the other at the bottom for draw-off of formaldehyde solution. When a ketone is present in the feed mixture, it collects in the decanting tank and is removed with the formaldehyde. It is however, possible to remove substantially pure ketone by equipping the column for fractional distillation such that the ketone vapour is withdrawn from the top of the column and the less volatile azeotropic mixture vapour is withdrawn at a point intermediate the feed mixture inlet and the ketone vapour outlet. To achieve substantially complete separation of ketone and formaldehyde under these conditions, it is preferred, if necessary, to adjust the quantity of water in the system so that it takes up all of the formaldehyde present. Any water required for this purpose is introduced at a point above the azeotrope condensation zone.

It is usually convenient to introduce the auxiliary product into the system separately from the feed mixture to be separated but it can be added to the feed mixture beforehand if desired.

The invention is illustrated by the following Examples; the percentages are by weight.

EXAMPLE I.

30 A mixture containing:
 90.4% of acetic acid
 4.5% of formic acid
 1.0% of formaldehyde
 4.1% of water

35 is introduced into a column provided at the top with a condenser and a decanting system.

40 Into the column there is introduced isopropyl ether intended to serve as auxiliary product. A heterogeneous aqueous phase is condensed at the top and decants. The aqueous mixture contains 28.2% of formaldehyde, 0.3% of auxiliary product and 0.01% of acids; the organic phase is returned into the column. At the bottom of

the column, a mixture of formic acid and acetic acid containing only 0.03% of formaldehyde and 0.05% of water is withdrawn. The acids of this mixture can be separated from one another by known means.

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EXAMPLE II.

Into a column provided with a decanting plate at a point midway of its height is introduced a mixture composed of:

acetic acid	55.4%	65
formic acid	13.5%	
acetone	18%	
formaldehyde	6.7%	
water	6.4%	

The column is charged with isopropyl acetate, as ketone auxiliary product. The mixture is introduced at the centre of the lower part of the column at the rate of 7 kg. per hour. 2 litres of water per hour are introduced at the middle of the upper part.

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1.150 kg. of acetone containing neither auxiliary product nor acids, and only 0.2% of formaldehyde and 0.2% of water are withdrawn per hour at the top of the column.

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On the decanting plate, there are separated the auxiliary product, which returns into the column, and an aqueous layer containing 15% of formaldehyde, 3% of acetone, 2% of auxiliary product and at most 0.05% of acids. From this mixture a pure formaldehyde solution can readily be obtained.

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At the bottom of the column, 4.91 kg. per hour of the mixture of formic acid and acetic acid containing only 0.1% of water and 0.05% of formaldehyde are withdrawn, from which mixture the pure formic acid and the pure acetic acid can be separated without difficulty.

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